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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
09/620,162	07/20/2000	Thomas H. Baum	249-Div.	2598

7590

06/24/2003

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EXAMINER

MARKHAM, WESLEY D

ART UNIT

PAPER NUMBER

1762

DATE MAILED: 06/24/2003

14

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary

Application N .

09/620,162

Applicant(s)

BAUM ET AL.

Examiner

Wesley D Markham

Art Unit

1762

-- The MAILING DATE of this communication appears on the cover sheet with the corresponding address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133).
- Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 21 April 2003.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-5,7-17,19,21 and 28-30 is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

- 5) ☐ Claim(s) _____ is/are allowed.

- 6) ☒ Claim(s) 1-5,7-17,19,21 and 28-30 is/are rejected.

- 7) ☐ Claim(s) _____ is/are objected to.

- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☒ The drawing(s) filed on 20 July 2000 is/are: a) ☒ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
- 11) ☐ The proposed drawing correction filed on _____ is: a) ☐ approved b) ☐ disapproved by the Examiner.
If approved, corrected drawings are required in reply to this Office action.
- 12) ☐ The oath or declaration is objected to by the Examiner.

Priority under 35 U.S.C. §§ 119 and 120

- 13) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
* See the attached detailed Office action for a list of the certified copies not received.
- 14) ☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. § 119(e) (to a provisional application).
a) ☐ The translation of the foreign language provisional application has been received.
- 15) ☒ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. §§ 120 and/or 121.

Attachment(s)

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☐ Information Disclosure Statement(s) (PTO-1449) Paper No(s) _____
- 4) ☐ Interview Summary (PTO-413) Paper No(s) _____
- 5) ☐ Notice of Informal Patent Application (PTO-152)
- 6) ☐ Other: _____

DETAILED ACTION

Response to Amendment

1. Acknowledgement is made of applicant's amendment E, filed as paper #13 on 4/21/2003, in which Claims 1, 17, 19, and 21 were amended, Claim 27 was canceled, and Claims 29 and 30 were added. Claims 1 – 5, 7 – 17, 19, 21, and 28 – 30 are currently pending in U.S. Application Serial No. 09/620,162, and an Office Action on the merits follows.

Drawings

2. The formal drawings (12 sheets, 12 figures) filed on 7/20/2000 are approved by the examiner.

Claim Objections

3. Claim 28 is objected to because of the following informalities: Claim 28, as presented by the applicant in amendment E, reads in part, "...wherein said manganate material is annealed in oxygen.14.". There appears to be a typographical error in this claim (i.e., the "14" at the end of the claim). Appropriate correction is required.

Claim Observations

4. The examiner notes that the transitional phrase "include", recited in Claims 3 – 5 of the instant application, has been interpreted to be equivalent to the transitional

phrase "comprise" (i.e., to be "open" language) because there is no indication in the applicant's specification / claims that the precursors for forming the doped A-site deficient manganate material are limited to the precursors explicitly listed in Claims 3 – 5.

Claim Rejections - 35 USC § 103

5. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

6. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).
7. After careful consideration, the rejection of Claims 1 – 5, 7 – 17, 19, 21, 27, and 28 under 35 U.S.C. 103(a) as being unpatentable over the combination of Li et al. (USPN 5,487,356) and Munakata et al. (USPN 6,060,420), and additionally, for

Claim 5 only, Vaartstra (USPN 6,010,969) and Biagini et al. (USPN 5,659,101), set forth in paragraphs 10 – 13 of the previous Office Action (i.e., the non-final Office Action, paper #12, mailed on 10/22/2002), is withdrawn. Specifically, the examiner notes that Munakata et al. is drawn to and teaches making A-site deficient manganate powder materials, while Li et al. teaches depositing similar manganate materials as films on a substrate by liquid delivery CVD. As such, there is no reasonable expectation that a powder material (such as the one taught by Munakata et al.) could or should be made by a CVD process that is designed to deposit a film on a substrate while preventing particle formation (i.e., the process of Li et al.).

8. Claims 1 – 4, 7 – 17, 19, 21, and 28 – 30 are rejected under 35 U.S.C. 103(a) as being unpatentable over Jin et al. (USPN 5,461,308) in view of Li et al. (USPN 5,487,356).
9. Regarding independent Claim 1 (from which Claims 2 – 4, 7 – 17, 19, 21, and 28 – 30 depend), Jin et al. teaches a method of forming a magnetoresistive, doped manganate material “21” on a substrate “20” (Figure 2 and Col.2, lines 11 – 19) by a technique such as chemical vapor deposition (Col.2, lines 41 – 46), the manganate material having the general formula $A_wB_xC_yO_z$, where A is preferably La (as claimed by the applicant); B is preferably Mg, Ca, Sr, or Ba (as claimed by the applicant); C is preferably Mn (as claimed by the applicant); $0.5 \leq w \leq 0.7$; $0.15 \leq x \leq 0.50$; $0.8 \leq y \leq 1.2$; and $2.7 \leq z \leq 3.3$ (Col.3, lines 33 – 44). The materials taught by Jin et al. have a Curie temperature of greater than or equal to 330 K (i.e., a value within the

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applicant's claimed range) (Col.3, lines 28 – 32). Further, the range of "y" values (i.e., the stoichiometric value of Mn) taught by Jin et al. (i.e., 0.8 to 1.2) encompasses the applicant's claimed stoichiometric value of Mn (i.e., 1), and the range of "z" values (i.e., the stoichiometric value of O) taught by Jin et al. (i.e., 2.7 to 3.3) encompasses the applicant's claimed stoichiometric value of O (i.e., 3). Jin et al. does not explicitly teach that the A-site filling value (i.e., the sum of "w + x" as defined in Jin et al., or, in the applicant's claimed terms, the sum of "x + y") is between 0.5 and 0.9. However, the ranges of "w" and "x" taught by Jin et al. lead to an A-site filling value of between 0.5 and 0.9, and thus the A-site deficient manganate material of the applicant's claims. For example, if the "x" value of Jin et al. (i.e., the stoichiometric value of Mg, Ca, Sr, or Ba) is chosen to be 0.15 (a preferred embodiment of Jin et al.) and the "w" value of Jin et al. (i.e., the stoichiometric value of La) is chosen to be any value from 0.5 to 0.7, inclusive, as preferred by Jin et al., an A-site filling value of from 0.65 to 0.85 is obtained. This value is within / encompassed by the applicant's claimed "x + y" value of between 0.5 and 0.9. Please note that, in the case where the claimed ranges overlap or lie inside ranges disclosed by the prior art, a *prima facie* case of obviousness exists (*In re Wertheim* 541 F.2d 257, 191 USPQ 90 (CCPA 1976); *In re Woodruff*, 919 F.2d 1575, 16 USPQ2d 1934 (Fed. Cir. 1990)). Also, a prior art reference that discloses a range encompassing a somewhat narrower claimed range is sufficient to establish a *prima facie* case of obviousness (*In re Peterson*, 315 F.3d 1325, 1330, 65 USPQ2d 1379, 1382-83 (Fed. Cir. 2003)). Jin et al. does not teach the specifics of the CVD

process that is utilized to deposit the magnetoresistive manganate material, specifically the step of liquid delivery and flash vaporization of precursor(s) to yield a precursor vapor, and transporting the precursor vapor to a CVD reactor for chemical vapor deposition formation of the manganate material on the substrate. Li et al. teaches a method of forming a doped, magnetoresistive manganate film on a substrate from corresponding precursors, the method comprising liquid delivery and flash vaporization of the precursors to yield a precursor vapor, and transporting the precursor vapor to a CVD reactor for the CVD formation of the manganate film on the substrate (Abstract, Figure 1, Col.3, lines 37 – 53, Col.7, lines 44 – 65, and Col.8, lines 30 – 52). Further, Li et al. teaches that their CVD method is used to deposit films having a giant magnetoresistance (GMR) effect, the films having a general formula $(La_{1-x}A_x)MnO_3$, wherein A is selected from the group consisting of Ba, Ca, Mn, and Sr (Abstract). In other words, Li et al. teaches that the liquid delivery / flash vaporization CVD process and apparatus can be successfully used to deposit magnetoresistive films (as desired by Jin et al.) having a composition almost identical to the films taught by Jin et al. (i.e., except for the A-site deficiency). In addition, Li et al. teaches that their CVD method is particularly attractive for forming these types of layers because (1) it is readily scaled up to production runs and the control of key variables such as oxygen partial pressure during deposition, film stoichiometry, and film thickness is most feasible with CVD (Col.2, lines 52 – 65), and (2) the controlled delivery of CVD reagents can be achieved (Col.3, lines 37 – 53). Therefore, it would have been obvious to one of ordinary skill in the art to

deposit the A-site deficient manganate materials of Jin et al. by using the liquid delivery / flash vaporization CVD process of Li et al. (i.e., the liquid delivery and flash vaporization of the precursors to yield a precursor vapor, and transporting the precursor vapor to a CVD reactor for the CVD formation of the manganate film on the substrate) with the reasonable expectation of (1) success, as Jin et al. teaches that the films can be deposited by CVD in general, and Li et al. teaches a specific type of CVD that is suitable to deposit magnetoresistive manganate films (i.e., such as the films taught by Jin et al.), and (2) obtaining the benefits of using the CVD process of Li et al. to deposit the films of Jin et al., such as the ability to readily scale up the process to production runs and to control key variables such as the delivery of the precursors, the oxygen partial pressure during deposition, the film thickness, and, importantly, the film stoichiometry.

10. The combination of Jin et al. and Li et al. also teaches all the limitations of Claims 2 – 4, 7 – 17, 19, 21, and 28 – 30 as set forth above in paragraph 9 and below, including a method wherein / further comprising:

- Claim 2 – The precursors comprise coordination compounds, or Lewis base complexes of metals selected from the group consisting of lanthanum, magnesium, calcium, strontium, barium, and manganese (Col.4, lines 12 – 68, Col.5, lines 1 – 45 and 65 – 67, and Col.6, lines 1 – 40 of Li et al.).

- Claim 3 – The precursors include metal β -diketonate compounds, metal pivalate compounds, or Lewis base complexes thereof (Col.6, lines 1 – 25, and Col.8, lines 30 – 52 of Li et al.).
- Claim 4 – The precursors include metal fluorinated β -diketonate compounds, or Lewis base complexes thereof (Col.6, lines 6 – 7 of Li et al.).
- Claim 7 – The precursors are dissolved in a solvent and flash vaporized at a temperature of from about 100° C to about 300° C (Col.6, lines 11 – 26, Col.7, lines 30 – 42, and Col.8, lines 30 – 52 of Li et al.). Specifically, Li et al. teach that a vaporizer temperature of 220° C is suitable (Col.7, line 37).
- Claim 8 – The precursor vapor is transported to the CVD reactor in a carrier gas (Col.7, lines 30 – 57, and Col.8, lines 30 – 52 of Li et al.).
- Claim 9 – The carrier gas is selected from the group consisting of argon, nitrogen, neon, helium, and ammonia (Col.6, lines 56 – 57, and Col.8, lines 47 – 48 of Li et al.).
- Claim 10 – The carrier gas is mixed with an oxidizing co-reactant gas in the CVD reactor or prior to transport to the CVD reactor (Col.6, lines 56 – 63, and Col.7, lines 44 – 56 of Li et al.).
- Claim 11 – The substrate in the CVD reactor is heated to a temperature in the range of about 300° C to about 1000° C (Col.7, lines 24 – 30, and Col.8, lines 49 – 51 of Li et al.).

- Claim 12 – The pressure of the precursor vapor in the CVD reactor is from about 0.1 to about 760 torr. Specifically, Li et al. teach reactor pressures of about 1.5 Torr (Col.7, line 35, and Col.8, lines 49 – 50).
- Claim 13 – The CVD is plasma-assisted (Col.7, lines 56 – 59 of Li et al.).
- Claim 14 – The precursors comprise a mixture of compounds selected from the group consisting of La(thd)₃, Ca(thd)₂, and Mn(thd)₃ (Col.8, lines 30 – 45 of Li et al.).
- Claim 15 – The precursors comprise a mixture of the compounds selected from the group consisting of La(thd)₃, Sr(thd)₂, and Mn(thd)₃ (Col.8, lines 30 – 45). Specifically, Li et al. teaches a mixture comprising La(thd)₃ and Mn(thd)₃.
- Claim 16 – The precursors comprise a mixture of Lewis base adducts of metal β -diketonate precursors (Col.6, lines 1 – 10 and 27 – 40 of Li et al.).
- Claim 17 – M is Ca and (La+Ca) < 0.9 in the A-site deficient manganate film. Specifically, Jin et al. teaches that “A” in their formula is La and “B” in their formula is Ca, as well as reasonably suggesting “A + B” (i.e., La + Ca) values of 0.65 to 0.85 (i.e., values in the range claimed by the applicant) (see paragraph 9 above).
- Claim 19 – M is Sr and (La+Sr) < 0.9 in the A-site deficient manganate film. Specifically, Jin et al. teaches that “A” in their formula is La and “B” in their formula is Sr, as well as reasonably suggesting “A + B” (i.e., La + Sr)

values of 0.65 to 0.85 (i.e., values in the range claimed by the applicant) (see paragraph 9 above).

- Claim 21 – M is Ba and $(La+Ba) < 0.9$ in the A-site deficient manganate film. Specifically, Jin et al. teaches that “A” in their formula is La and “B” in their formula is Ba, as well as reasonably suggesting “A + B” (i.e., La + Ba) values of 0.65 to 0.85 (i.e., values in the range claimed by the applicant) (see paragraph 9 above).
- Claim 28 – The manganate material is annealed in oxygen. Specifically, Jin et al. teaches that the manganate material should have a high Curie temperature, such as above 330 K (Col.3, lines 28 – 32). Li et al. teaches that the properties of the magnetoresistive films deposited by their invention (i.e., films similar to those deposited by Jin et al.) can be improved by post-growth annealing in an oxidizing atmosphere (Col.8, lines 4 – 8). Particularly, Li et al. teaches that annealing the manganate films in O₂ increases the Curie temperature of the films (Col.8, lines 58 – 61). Therefore, it would have been obvious to one of ordinary skill in the art to anneal the films deposited by the method of the combination of Jin et al. and Li et al. in oxygen (as taught by Li et al.) with the reasonable expectation of successfully and advantageously improving the properties of the film(s), such as increasing the Curie temperature of the films, in order to achieve a high Curie temperature as desired by Jin et al.

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- Claim 29 – The (La + Ca):Mn ratio is between 0.6 and 0.9. Specifically, Jin et al. reasonably suggests (La + Ca) values of from 0.65 to 0.85, which are within the applicant's claimed range, when compared to an Mn value of 1 (see discussion of Claim 17 above).
- Claim 30 – The Ca/La ratio is between 0.35 and 0.55. Specifically, Jin et al. teaches that "A" in their formula is La and "B" in their formula is Ca (Col.3, lines 33 – 39). Jin et al. also teaches "x" values (i.e., the stoichiometric value of Ca) of from 0.15 to 0.50, inclusive, and "w" values (i.e., the stoichiometric value of La) of from 0.5 to 0.7, inclusive (Col.3, lines 29 – 41). Therefore, by selecting an "x" value in the preferred range taught by Jin et al., for example $x=0.2$, and a "w" value in the preferred range taught by Jin et al., for example $w=0.5$, a Ca/La ratio of $0.2/0.5 = 0.4$ is obtained. This value is within the applicant's claimed range.

11. Claim 5 is rejected under 35 U.S.C. 103(a) as being unpatentable over Jin et al.

(USPN 5,461,308) in view of Li et al. (USPN 5,487,356), and in further view of Vaartstra (USPN 6,010,969) and Biagini et al. (USPN 5,659,101).

12. The combination of Jin et al. and Li et al. teaches all the limitations of Claim 5 as set forth in paragraph 9 above, except for a method wherein the precursors include metal pivalate Lewis base adducts. However, Li et al. does teach that suitable ligands that are used in the metal / ligand precursors of their invention include beta-diketonates. In addition, Li et al. teaches that Lewis base complexing components

that coordinate with the metal centers of the precursors are used to increase the volatility of the source reagents and to facilitate their transport to the CVD reactor (Col.6, lines 1 – 10 and 27 – 40). Vaartstra teaches that, in the art of forming oxide films by flash vaporization CVD on a substrate (Col.1, lines 40 – 58, Col.2, lines 1 – 8, and Col.3, lines 1 – 45), it was known at the time of the applicant's invention to use carboxylate ligands such as pivalate ligands in metal-containing CVD precursors (Col.3, lines 46 – 57). Other ligands such polyamines (i.e., a Lewis base compound) can also be complexed to the metal to increase the precursor's volatility (Col.3, lines 58 – 67). Vaartstra also teaches that a wide variety of metals can be successfully complexed with the carboxylate ligands (Col.5, lines 52 – 61). Biagini et al. teaches the functional equivalence of ligands such as acetylacetonate and hexafluoroacetylacetonate (i.e., ligands taught by Li et al. for use in their CVD process) and pivalate ligands (Col.3, lines 39 – 53). It would have been obvious to one of ordinary skill in the art to utilize metal pivalate Lewis base adducts as taught by Vaartstra as precursors in the CVD process of the combination of Jin et al. and Li et al. with the reasonable expectation of success and with the expectation of similar results (i.e., successfully forming the manganate film on a substrate, regardless of whether a β -diketonate precursor is used or a metal pivalate Lewis base adduct is used as the precursor).

Response to Arguments

13. The applicant's arguments filed on 4/21/2003 have been fully considered but are not persuasive. Specifically, the arguments are moot in view of the new grounds of rejection presented above.

Conclusion

The prior art made of record and not relied upon is considered pertinent to applicant's disclosure. Von Helmolt et al. (USPN 5,563,331) teaches manganate films exhibiting magnetoresistance.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Wesley D Markham whose telephone number is (703) 308-7557. The examiner can normally be reached on Monday - Friday, 8:00 AM to 4:30 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Shrive Beck can be reached on (703) 308-2333. The fax phone numbers for the organization where this application or proceeding is assigned are (703) 872-9310 for regular communications and (703) 872-9311 for After Final communications.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is (703) 308-0661.


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WDM
June 18, 2003

Wesley D Markham
Examiner
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TIMOTHY MEEKS
PRIMARY EXAMINER